



SECTION 2 ASPHALT EMULSION THEORY

2.1 Overview

Asphalt emulsions, used in road construction and maintenance, may be defined as a homogeneous mixture of minute asphalt droplets suspended in a continuous water phase. These types of emulsions are usually termed oil-in- water (o/w) emulsions. Their preparation involves the use of a high speed, high shear mechanical device, such as a colloid mill. The colloid mill breaks down molten asphalt into minute droplets in the presence of water and a chemical, surface active emulsifier. The emulsifier imparts its properties to the dispersed asphalt and is most influential in maintaining stable asphalt droplet suspension.

Asphalt emulsions are classified into three categories; anionic, cationic, and nonionic. In practice, the first two types are ordinarily used in roadway construction and maintenance. The anionic and cationic classes refer to the electrical charges surrounding the asphalt particles. This identification system stems from one of the basic laws of electricity; like charges repel one another and unlike charges attract. When two poles (an anode and a cathode) are immersed in a liquid and an electric current is passed through, the anode becomes positively charged and the cathode becomes negatively charged.

If a current is passed through an emulsion containing negatively charged particles of asphalt they will migrate to the anode. Hence, it is referred to an anionic.

Conversely, positively charged particles will move to the cathode and is referred to as cationic. With non ionic emulsions, the asphalt particles are neutral and, therefore, do not migrate to either pole.

The polarity of the asphalt emulsion is determined by the type of the emulsifying agent used. If the surfactant, often called the emulsifier, inherently possesses a negative charge, the asphalt droplets bear a negative charge. If the surfactant inherently possesses a positive charge, the asphalt droplets bear a positive charge. In nonionic emulsions the asphalt particles have a neutral charge.

The three primary chemical components of emulsion, asphalt, water, and emulsifier, joined together by the mechanical influence of a colloid mill, are the necessary ingredients in the chemistry and related production of paving asphalt emulsions. Other additives may be incorporated to fulfill a specific purpose.

2.2 Asphalt

Asphalt cement is the basic ingredient of an asphalt emulsion. It makes up from 50 to 75% of the emulsion, although, in most cases, the range is from 55 to 70%.



Asphalt chemistry is a complex subject, and there is no need to examine all of the properties of asphalt cement. Only those that affect emulsions are discussed. Some properties of the asphalt cement significantly affect those of the finished emulsion. There is not an exact correlation, however, between the properties and the ease with which the asphalt can be emulsified. Although hardness of base asphalt cements may vary, most emulsions are made with asphalts in the 100 to 250 penetration range. On occasion, climatic conditions may dictate that a harder or softer base asphalt be used. In any case, compatibility of the emulsifying agent with the asphalt cement is essential for production of a stable emulsion.

Asphalt is a colloid composed of several fractions, the major ones being asphaltenes and maltenes. The colloidal makeup of the asphalt depends on the chemical nature and percentage of ratio of these fractions and their relationship to each other. The varying chemical and physical characteristics of asphalt are primarily due to inherent variations in crude oil sources and refining practices.

The asphaltenes are the dispersed phase in the asphalt whereas the maltenes are the continuous phase. Asphaltenes are insoluble in n-pentane and have a fairly high molecular weight. The maltene fraction is composed of sub-fractions of oil and resins.

The asphaltenes are thought to furnish hardness while the maltenes are believed to endow the adhesive and ductile properties of the asphalt. The oils and resins present have an influence on the viscosity, or flow properties, of the asphalt. The complex interaction of the different fractions make it almost impossible to predict accurately the behavior of an asphalt to be emulsified. Asphalts, even from the same refinery, vary in behavior. This is confirmed by the differences in the emulsions manufactured from the asphalts through tests such as: viscosity, pump stability (do not break down while pumping), and general stability (do not break down during storage or while handling)

Several systems of asphalt analysis are in use today to separate and evaluate the fractions. There is no absolute agreement among technologists as to how each fraction affects field performance. Nor is there total agreement about the ease with which an asphalt cement can be emulsified.

Emulsion manufacturers determine their own formulations and production techniques, that have been developed to achieve optimum results with the asphalt cement and emulsifying chemicals available.

2.3 Water

The second largest ingredient in an asphalt emulsion is water. Its contribution to the desired properties of the finished product cannot be minimized. Water may contain minerals or other matter that helps or hurts the production of stable asphalt emulsions. Accordingly, water considered pure for drinking might not be pure for use in asphalt emulsion.

Water wets and dissolves. It adheres to other substances. And it moderates chemical reactions. Those are all important factors that can be favorable to the production of a satisfactory emulsion.

Water found in nature may be unfit because of impurities, either in solution or colloidal suspension. Of particular concern is the presence of calcium and magnesium ions. These ions benefit the formation of a stable cationic emulsion. In fact, calcium chloride is often added to cationic emulsions to enhance storage stability.



These same ions, however, can be harmful in anionic emulsions. That is because water insoluble calcium and magnesium salts are formed from the reaction with water soluble sodium and potassium salts normally used as organic emulsifiers.

In a like manner, carbonate and bicarbonate ions can help produce an anionic emulsion because of their buffering effect. But they probably would suppress a stable cationic emulsion. That is because of their reaction with the water soluble amine hydrochlorides which are often used as a cationic emulsifier.

Water containing particulate matter should not be used in emulsion production. It can be especially harmful in cationic emulsions. The usually negatively charged particles quickly adsorb the cationic emulsifying agents. The result is an imbalance of the emulsion components that can adversely affect emulsification and performance.

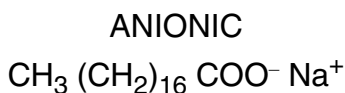
2.4 Emulsifying Agents (Surfactants)

Asphalt emulsion properties depend greatly upon the chemical used as the emulsifier. That chemical is a surface active agent, commonly called surfactant. It is the determining factor as to whether the emulsion will be classified as anionic, cationic, or nonionic. The emulsifier also keeps the asphalt droplets in stable suspension and permits the asphalt to be deposited onto the aggregate at the proper time.

By broad definition surface active chemicals are water soluble substances whose presence in solution markedly changes the properties of the solvent and the surfaces they contact. They are categorized according to the manner in which they dissociate or ionize in water and are characterized, structurally, by possessing a molecular balance of a long lipophilic, hydrocarbon tail and a polar, hydrophilic head. Surface active agents owe their physiochemical behavior to their property of being adsorbed at the interface between liquids and gases or liquid and solid phases. They tend to concentrate in an oriented manner, at the interface, in such a way that, almost entirely, they turn a majority of their hydrophilic groups toward the more polar phase and a majority of their lipophilic groups away from the more polar phase and perhaps even into a non polar medium. The surface active molecule or ion, in a sense, acts as sort of a bridge between two phases and makes any transition between them less abrupt.

Basically, there are three types of chemical surface active agents which are classified according to their dissociation characteristics in water. They are:

1. Anionic Surfactants-where the electrovalent and polar hydrocarbon group is part of the negatively charged ion, when the compound ionizes:



2. Nonionic Surfactants — Where the hydrophilic group is covalent and polar and which dissolves without ionization:

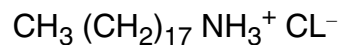


NONIONIC



3. Cationic Surfactants — Where the electrovalent and polar hydrocarbon group is part of the positively charged ion when the compound ionized:

CATIONIC



Alternately called surface active chemical or surfactant, the emulsifier is the single most important component in any paving asphalt, oil-in-water emulsion formulation. To be an effective emulsifier for asphalt, a surfactant must be water soluble and must possess a proper balance between the hydrophilic and lipophilic properties inherently found in each true surfactant-type chemical. The emulsifier, when used in combination with an acceptable asphalt, good quality water and adequate mechanical input, is the major factor which influences initial emulsification, emulsion stability and ultimate field application performance. A wide range of chemical emulsifiers are available.

Each manufacturer has its own procedure for using surfactants in asphalt emulsion production. In most cases, the surfactant is combined with the water before introduction into the colloid mill. However, it may be combined with the asphalt cement just before it goes into the colloid mill.

The rate at which the asphalt emulsion is deposited onto an aggregate surface as asphalt cement is controlled, largely, by the specific type and concentration of the emulsifying agent being used. This chemically controlled feature of asphalt emulsions relates to the availability of three cationic and noncationic emulsion grades: rapid, medium and slow setting as designated in ASTM D997 and D2397 and MSHTO M-140 and M-208.

Factors which affect the setting rate or rate of asphalt deposition (RAD) of an asphalt emulsion:

- Water Absorption — The rate that water is absorbed by the aggregate and old pavement or base, or worn pavement speeds the setting time by absorbing water from the emulsion.
- Weather Conditions — Temperature, humidity, and wind velocity all have a bearing on rate of asphalt deposition onto an aggregate surface since they affect water evaporation rate and emulsifier migration and water release characteristics.
- Mechanical Forces — Forces brought to bear by rolling and by traffic. Roller pressure, to some extent, forces the water from the mix and helps attainment of mix cohesion, cure and stability.
- Surface Area — Size distribution, dirty aggregate and excessive fines may accel-



erate the rate at which asphalt is deposited onto the aggregate (break time).

- **Surface Charge** — The intensity of the negative surface charge on aggregates may affect the rate of asphalt deposition onto an aggregate surface from cationic emulsions. High aggregate surface charge causes more rapid deposition.
- **Emulsion and Aggregate Temperature** — Cool emulsion and aggregate temperature usually retards setting (rate of asphalt deposition) time. Warm or hot emulsion and aggregate temperature accelerates RAD.
- **Type and Amount of Emulsifier** — The emulsifier used in the manufacture of the emulsion and the amount used can affect rate of asphalt deposition.

The above factors must be considered in determining working time after the emulsion has been sprayed or mixed with the aggregate in the field.

2.5 References:

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